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Origin of the Negative Shift of Half-Wave Reduction Potentials of Aromatic Polynuclear *p*-Quinones with Increasing Conjugation[1]

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The half-wave reduction potentials ($E_{1/2}^{\text{red}}$) of aromatic polynuclear *p*-quinones are negative shifted with increasing π-electron conjugation, although the $E_{1/2}^{\text{red}}$ values of usual organic substances are positive shifted with the above structure change. The main reason for this exceptional behavior of the *p*-quinones has been discussed in detail by applying the composite system method (linear combination of molecular orbitals (LCMO) approximation). For example, after dividing naphthoquinone into benzoquinone and *cis*-butadiene we consider the mutual interaction between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the former and those of the latter. It was concluded that the interaction between the LUMO of the former and the HOMO of the latter plays an important role, so that the LUMO of benzoquinone is destabilized by going to naphthoquinone, leading to the negative shift of $E_{1/2}^{\text{red}}$ value.

Keywords——half-wave reduction potential; aromatic polynuclear *p*-quinone; aromatic polynuclear *o*-quinone; polyacene; polynuclear *p*-hydroquinone; *p*-diazapolyacene di-*N*-oxide; HOMO–LUMO interaction; LCMO; composite system method; *ab initio*-semiempirical-MO calculation

In studies of organic polarography the relation between half-wave reduction or oxidation potential and molecular structure is an important problem, and various kinds of investigations have been carried out.[2–9] From these studies, it is well known that the first half-wave reduction potential ($E_{1/2}^{\text{red}}$) of usual organic compounds shows a positive shift (*i.e.*, easier reduction) with increasing π-electron conjugation. A typical example is a series of polyacenes (alternant hydrocarbons such as benzene, naphthalene, anthracene, *etc.*).[2–4,10,11] However, in the course of aqueous and nonaqueous polarographic studies of organic substances we found that the $E_{1/2}^{\text{red}}$ values of aromatic *p*-quinones show a negative shift with increasing ring size along the *Z*-axis, as shown in Chart 1, in contrast with a series of di-*N*-oxides of pyrazine, quinoxaline, phenazine, *etc.*, the reduction potentials of which are positive shifted with increasing ring size.[12] Many quinone compounds are physiologically active substances, such as antibiotics, antitumor agents, and vitamin K group.[13] That the oxidation–reduction process of these quinone substances plays an important role in the physiological activities in biological systems is easily inferred.[14] Further, the reduction or oxidation potential of a series

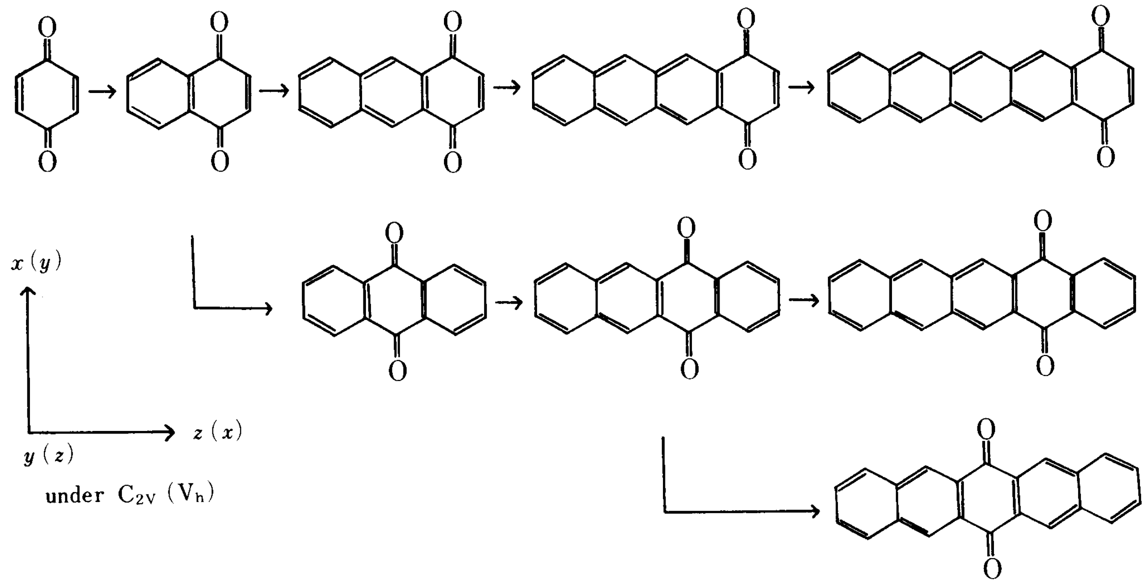

Chart 1. Structure Change of Aromatic Polynuclear *p*-Quinones Studied

The coordinate axes used for MO calculations are shown for C_{2v} and V_h symmetries, the axis for the latter being given in parentheses.

of drugs is an important electronic parameter in studies of quantitative structure activity relationships.[15] Thus, we were interested in the origin of the apparently abnormal behavior of aromatic *p*-quinones as regards the correlation between reduction potential and molecular structure. It should be noted that the π-electron systems of the above *p*-quinones and di-*N*-oxides are only distinguished in that the latter has two extra π-electrons compared with the corresponding compound in the former group, despite having the same molecular symmetry. It is therefore conceivable that some topological feature such as the orbital symmetry and the number of π-atomic orbitals (π-AO) and π-electrons is different for the *p*-quinone series as compared with other molecules such as the above di-*N*-oxides, and this causes the unusual behavior of the $E_{1/2}^{\mathrm{red}}$ values of the *p*-quinone series. These problems are discussed in this paper.

Experimental

Polarographic Measurement——Nonaqueous reduction potentials of various kinds of polynuclear aromatic *p*-quinones were measured with a Yanagimoto polarograph (model P-1000), using a dropping mercury electrode and a saturated calomel electrode (SCE) as the working and reference electrodes, respectively.[5,6,12,16] Reversibility of the reduction potentials was checked by recording the cyclic voltammogram. All the experiments were carried out at $25.0 \pm 0.1\,^{\circ}\mathrm{C}$ in *N*,*N*-dimethylformamide (DMF) containing $0.1\,\mathrm{mol\ dm^{-3}}$ tetrapropylammoniumperchlorate (TPAP), sample concentrations being *ca.* $5 \times 10^{-4}\,\mathrm{mol\ dm^{-3}}$. Details of nonaqueous polarographic and cyclic voltammetric measurements and the purification method for DMF and TPAP were given in the foregoing papers.[5-7,14]

Molecular Orbital Calculation——In order to interpret the $E_{1/2}^{\mathrm{red}}$ values, molecular orbital (MO) calculations were carried out. As discussed in a later section, the π-MO levels and their symmetries in the neighborhood of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) may be important. The MO calculation was therefore performed by three different but widely used methods, applicable to large molecules, in order to check whether consistent results could be obtained. The methods used were the Pariser-Paar-Pople (PPP) type SCF-MO, which leads to quite a good result for the π-electron system alone, CNDO/2 for all valence semiempirical calculations, and *ab initio* SCFMO at the STO-3G level. The PPP method was applied to all the molecules studied, and the results were compared and checked by CNDO/2 or STO-3G calculation for fundamental substances. Although the reliability of STO-3G calculation seems to be less for vacant orbitals[17a] than occupied ones, we have done this calculation in order to compare the *ab initio* calculation results on orbital nature with the PPP and CNDO/2 semiempirical ones. Details of the PPP and CNDO/2 methods have already been discussed.[5,6] We used the

TABLE I. Aromatic Polynuclear *p*-Quinones and *cis*-Butadiene Investigated, with Melting Points, Half-Wave Reduction Potentials in DMF, and HOMO and LUMO π-Energies Calculated by Three Different MO Methods

Compounds	mp (°C)	$E_{1/2}^{\text{red}}$[a] (V *vs.* SCE)	LUMO energy (eV)				HOMO energy (eV)			
			PPP	CNDO/2	STO-3G	Sym[b]	PPP	CNDO/2	STO-3G	Sym[b]
p-Benzoquinone	116.5—117.5	−0.481	−4.084	−0.290	3.565	a_2 (b_{3g})	−10.880	−12.789	−7.863	b_2 (b_{1u})
Naphthoquinone	124.4—125.0	−0.656	−3.766	0.157	3.856	a_2	−10.716 −10.785	−12.660 −14.052	−7.635 −8.052	b_2 a_2 [d]
Anthraquinone	287.0—289.0	−0.888	−3.452	0.579	4.139	a_2 (b_{3g})	−10.610 −10.707	−12.553 −13.618	−7.505 −7.861	$b_2(b_{1u})$ $a_2(b_{3g})$ [d]
1,4-Anthraquinone			−3.619			a_2	−9.663			a_2
1,4-Naphthacenequinone			−3.568			a_2	−9.010			a_2
5,12-Naphthacenequinone	286—290	−0.995	−3.340	0.820	4.278	a_2	−9.602	−11.104	−6.014	a_2
1,4-Pentacenequinone			−3.706 −3.545			b_2 a_2 [c]	−8.590			a_2
6,13-Pentacenequinone			−3.213			a_2 (b_{3g})	−9.579			a_2 (a_u)
cis-Butadiene			−2.123		6.643	b_2	−9.717		−7.070	a_2

[a] Reduction waves corresponding to these potentials show good reversibility for all the quinones from the viewpoint of cyclic voltammetric measurement. [b] Orbital symmetry is denoted under C_{2v} and V_h, the latter being given in parentheses. [c] Next LUMO energy is also listed. [d] Next HOMO energy is also listed.

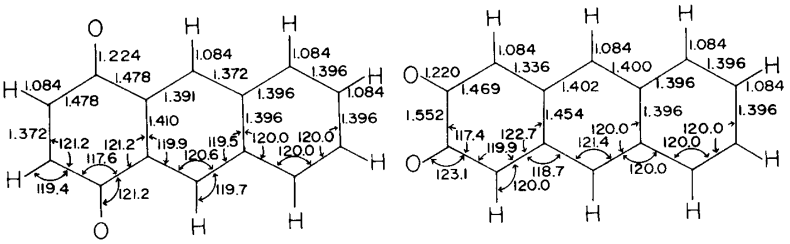

Fig. 1. Molecular Dimensions Employed for MO Calculations of 5,8-Anthraquinone and 6,7-Anthraquinone as Two Typical Examples among Various Quinone Compounds

See the text for details.

Table II. Half-Wave Reduction Potentials in DMF of Anthraquinones Substituted at the 1 or 2 Position, with Their Melting Points, Hammett's σ_p Substituent Constant, and LUMO π-Energies Calculated by the PPP-SCFMO Method

Compounds	mp (°C)	$E_{1/2}^{\mathrm{red}\,a)}$ (V *vs.* SCE)	σ_p	LUMO energies (eV)
Anthraquinone	287.0—289.0	-0.888	0.000	-3.452
1-Chloroanthraquinone	164.0—165.0	-0.829		-3.441
1-Bromoanthraquinone	192.0—193.0	-0.823		
2-Methylanthraquinone	177.0—178.5	-0.902	-0.170	-3.412
2-Ethylanthraquinone	111.5—112.0	-0.919	-0.15	
2-Fluoroanthraquinone	201.0—203.5	-0.820	0.062	
2-Chloroanthraquinone	213.5—214.5	-0.790	0.227	-3.434
2-Bromoanthraquinone	210.5—211.0	-0.787	0.232	
2-Aminoanthraquinone	>300	-1.063	-0.660	-3.287

a) Reduction waves corresponding to these potentials show good reversibility for all the quinones as determined by cyclic voltammetry.

Nishimoto–Mataga (NM) approximation[17b] for two-center repulsion integrals. As regards the parameters in PPP calculation, the ionization potential (I_p) and electron affinity (E_A) in the valence state of all the atoms are the same as reported in our foregoing papers.[5-7] The core resonance integrals (β_{core}) in the quinone moiety were -2.00, -2.50, and -2.50 eV for C–C, C=C, and C=O bonds, respectively (taken from the paper by Kuboyama and Matsuzaki).[18] The β_{core} values of the C–C bond in the aromatic ring, except for a *p*- or *o*-type quinone ring, are the same (-2.37 eV) as in our previous papers.[5-7] We have used the IMS library program "IMSPACK" written by Morokuma and his group at the Institute for Molecular Science for the *ab initio* calculation of STO-3G basis sets.

Molecular dimensions were determined by referring to the results of X-ray crystallographic analysis for anthraquinone[19a] and *o*-benzoquinone[19b] but were modified slightly to retain molecular symmetry (C_{2v} or V_h), for convenience. Figure 1 shows the molecular dimensions for representative quinone compounds, 5,8-anthraquinone and 6,7-anthraquinone, where a regular hexagon of 1.396 Å was assumed for the aromatic rings separated by more than two rings from a quinone moiety. In the case of the MO calculation of a series of polyacenes we always assumed a condensed regular hexagon system with values of 1.396 and 1.084 Å for the C–C and C–H distances, respectively.[20] PPP and CNDO/2 calculations were carried out on a FACOM M-382 computer at the Nagoya University Computation Center, and *ab initio* calculations were done on a FACOM M-200H computer at the Institute for Molecular Science.

Samples——Quinones employed for the present experiments and their melting points are listed in Tables I and II; *p*-benzoquinone (BQ), naphthoquinone (NQ), anthraquinone (AQ), and 5,12-naphthacenequinone (NTQ) are commercially available. NQ, AQ, and NTQ were repeatedly purified by reduced-pressure or high-vacuum sublimation. Recrystallization from ligroin, ether, and ethanol was applied to purify BQ. 2-Substituted AQ's with F, Cl, Br, CH_3, C_2H_5, and NH_2 groups, and 1-substituted AQ's with Cl and Br are the same as those used for the spectroscopic study by Kuboyama and his coworkers.[21] The elemental analysis data for all the samples agreed well with the calculated values.

Results and Discussion

Structure Dependence of Nonaqueous Reduction Potentials of Aromatic Polynuclear *p*-Quinones

In earlier papers, it was shown that the first $E^{\mathrm{red}}_{1/2}$ value due to the anion radical formation and the LUMO energy ($\varepsilon_{\mathrm{1u}}$) are in the relation described by Eq. 1,[5,6,22-24] where $\Delta E^{\dot{-}}_{\mathrm{solv}}$ is the solvation energy difference between the anion radical and neutral species. The absolute potential of the reference electrode is expressed as ΔG° and is constant in the same experimental system.[5,24]

$$FE^{\mathrm{red}}_{1/2} = -\varepsilon_{\mathrm{1u}} - \Delta E^{\dot{-}}_{\mathrm{solv}} + \Delta G^{\circ} \qquad (1)$$

If the solvation energy term $\Delta E^{\dot{-}}_{\mathrm{solv}}$ is almost constant or alters in parallel to the change of $\varepsilon_{\mathrm{1u}}$ in a series of substances, then $E^{\mathrm{red}}_{1/2}$ and $\varepsilon_{\mathrm{1u}}$ should be in a linear relation. The $E^{\mathrm{red}}_{1/2}$ and $\varepsilon_{\mathrm{1u}}$ values

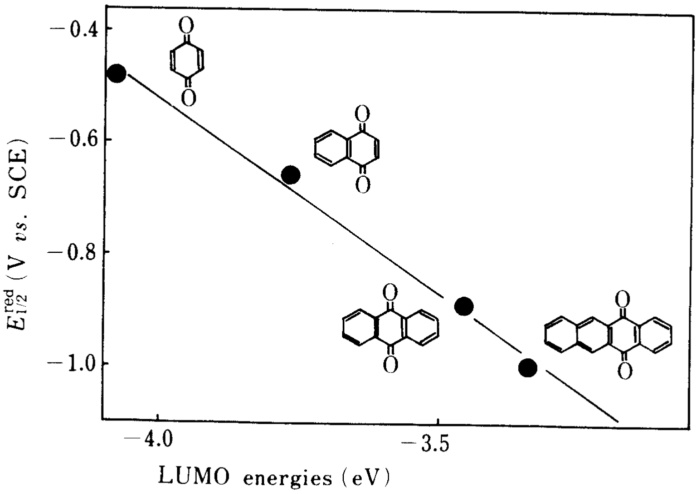

Fig. 2. Correlation of Nonaqueous $E^{\mathrm{red}}_{1/2}$ Values of *p*-Quinones to the PPP π-LUMO Energies

See Eq. 1 for the theoretical background. The least-squares equation is $E^{\mathrm{red}}_{1/2} = -0.687\varepsilon_{\mathrm{1u}} - 3.271$ with *r* (correlation coefficient) = 0.9954.

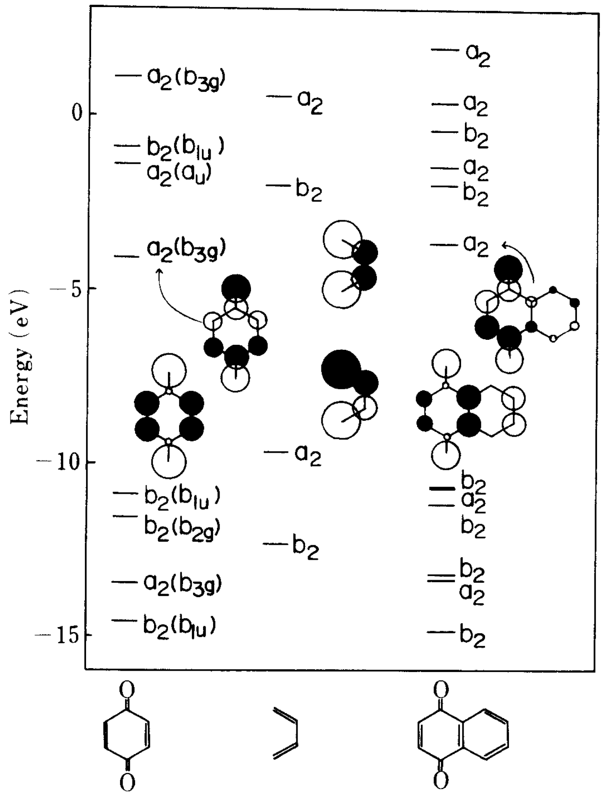

Fig. 3. PPP π-MO Energy Levels and the MO Illustration of HOMO's and LUMO's of *p*-Naphthoquinone and Its Composite System Consisting of *p*-Benzoquinone and *cis*-Butadiene

The axes under C_{2v} and V_h are given in Chart 1.

for the quinones studied here are listed in Tables I and II (three calculation methods were applied to get the ε_{1u} values). Figure 2 shows an example of the linear relation of $E^{\rm red}_{1/2}$ to ε_{1u} for *p*-quinone substances. Note that although the above linear relation is quite good, the reduction potential shifts to a more negative value with increasing conjugation along the *Z*-axis. We will discuss this problem in comparison with the cases of series of polyacenes, heterocyclic *N*-oxides, *p*-hydroquinones, *etc.*, in which the reduction potentials are positive shifted by increasing π-conjugation (this is chemically well-known behavior). The concept of the linear combination of molecular orbitals (LCMO)[25,26] based on the perturbation theory has been applied to solve this problem by using the PPP-SCFMO, CNDO/2, and *ab initio* STO-3G methods. The *p*-quinones are divided into *cis*-1,3-butadiene (BD) and the residual quinone systems, and then the mutual interaction between the systems is considered by focusing attention on the behavior of π-type LUMO and HOMO energies, since the reduction product at the nonaqueous half-wave reduction potential of all the substances discussed in this paper is well known to be a π-type anion radical, based on electron spin resonance study.[12,27,28] The π-MO energy of BQ (a fundamental substance) calculated by the PPP method is illustrated in Fig. 3, where each MO symmetry is given under both the molecular symmetrices, C_{2v} and V_h. Note that the ordering of each π-MO in Fig. 3 is the same among the three different MO calculations mentioned above, though the MO energies themselves are quite different among the three methods (see Table I). The same result as regards the π-MO

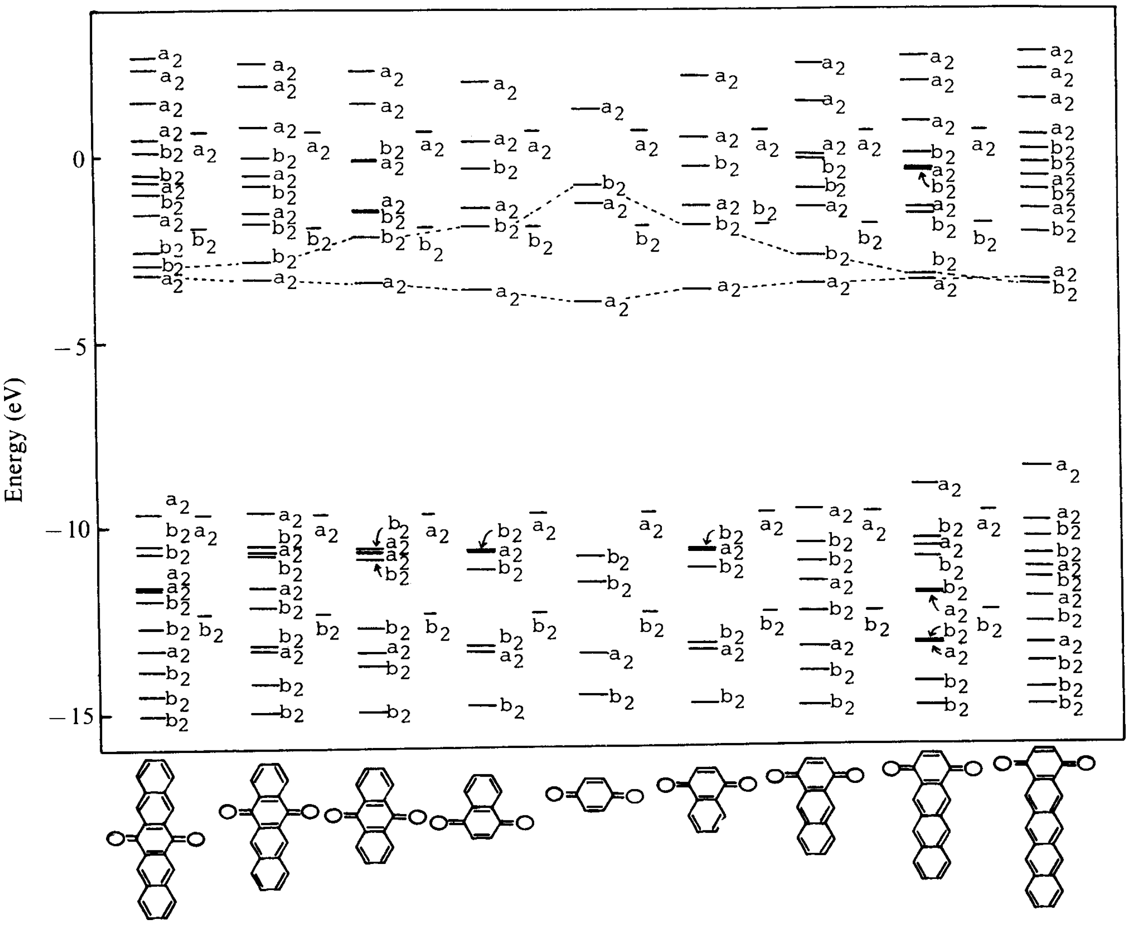

Fig. 4. Change of PPP π-MO Energy Levels of *p*-Quinone with Increasing Ring Size along the *Z*-axis under C_{2v}

The shift of a_2 and b_2 LUMO's of *p*-quinone due to the structure change is indicated by the dotted line. The energy levels inserted between any two quinones are those for *cis*-butadiene. The axis under C_{2v} is given in Chart 1.

ordering in the three different MO calculations was also obtained for the other series of compounds discussed in this report. The electronic structure of BQ has been studied in detail by various kinds of spectroscopic methods.[29-31] As regards the vacant orbitals, these experimental and theoretical investigations indicated that the LUMO having b_{3g} symmetry is considerably stabilized and has contributions from the carbonyl group oxygen atoms with different sign (see Fig. 3); in other words, this LUMO may originate mainly from the contribution of >C=O groups in BQ. The LUMO energies calculated by the three different methods are listed in Table I. However, the ordering of the two middle vacant π orbitals, a_u and b_{1u}, is not fixed at present. A recent study using electron transmission spectroscopy provided evidence that b_{1u} is below a_u,[31] just the reverse of the calculation result seen in Fig. 3,[32] in which the MO energies of BD are also shown. The HOMO and LUMO of the BD molecule have the symmetry of a_2 and b_2 under C_{2v}, respectively, and the HOMO of BD is shallower than the HOMO of BQ with the symmetry b_2 (b_{1u} under V_h). Now, let us discuss the molecular electronic states of aromatic polynuclear *p*-quinones under C_{2v} symmetry, because all the quinones discussed here have at least C_{2v} symmetry. The LUMO and HOMO energies of NQ may be constructed by considering the mutual interaction of the MO's of BQ and BD. Keeping in mind that only the Mo's having the same symmetry can interact with one another, and referring to Fig. 3, we can easily understand that the a_2 LUMO of BQ can not interact with the LUMO (b_2) of BD. The main interaction of the LUMO of BQ may occur through the a_2 HOMO of BD.[33,34] This interaction is also favored by the fact that the latter is much shallower in terms of energy than the HOMO and its adjacent orbital energies of BQ (see Fig. 3). As a result, the LUMO (a_2) of NQ is unstabilized in comparison with the LUMO of BQ. This kind of interaction is always found in other aromatic *p*-quinones and BD, as is illustrated in Figs. 3 and 4, from which we see that the a_2 type LUMO of aromatic *p*-quinones becomes shallower in energy with increasing ring size along the *Z*-axis, and the HOMO of the quinones turns out to have a_2 symmetry and shallow character in line with the behavior of the LUMO. These facts suggest strongly that the $E_{1/2}^{\text{red}}$ value due to the LUMO of BQ becomes more negative with increasing ring size (*i.e.* reduction is more difficult). On the other hand, it

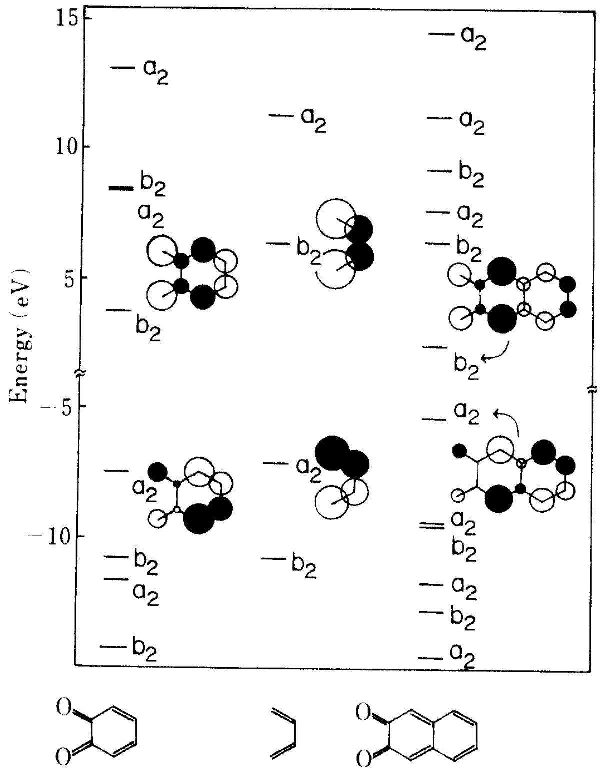

Fig. 5. STO-3G π-MO Energy Levels and the MO Illustration of π-HOMO's and π-LUMO's of *o*-Naphthoquinone and Its Composite System Consisting of *o*-Benzoquinone and *cis*-Butadiene

The axis under C_{2v} is given in Chart 1.

appears likely that the b_2 LUMO of BD would be located at lower energy than the unoccupied b_2 π-MO of BQ, and the mutual interaction of these two b_2 orbitals may mean that the penultimate LUMO of NQ is b_2 with deeper energy than that in BQ (see Fig. 4). This kind of b_2 type interaction may give rise to shift the b_2 unoccupied MO of *p*-quinones quite markedly to deeper energy with increasing ring size along the *Z*-axis. Thus, the calculation results in Fig. 4 indicate that the LUMO of 1,4-pentacenequinone may be a b_2 orbital having hydrocarbon character, so that at this stage we can easily predict a positive shift of $E^{\mathrm{red}}_{1/2}$ value with increasing ring size.

Behavior of Reduction Potentials of Aromatic Polynuclear *o*-Quinones

The calculation of aromatic *o*-quinones seems to be very interesting in comparison with the case of the *p*-quinone series, since *p*-quinones and *o*-quinones are isoelectronic for the π-electron systems. Figure 5 illustrates the MO's and their energy levels of *o*-naphthoquinone (ONQ), *o*-benzoquinone (OBQ), and BD. The calculation results are given in Table III. Here it should be noted that the symmetry of the LUMO and HOMO of OBQ is b_2 and a_2, respectively, and just the reverse of those of BQ. This indicates that the b_2 LUMO of OBQ interacts quite strongly with that (b_2) of BD, resulting in stabilization of the LUMO of OBQ on going from OBQ to ONQ, as is actually found in Fig. 5. The same interaction as above is also considered to occur between the a_2 HOMO's of OBQ and BD, so the a_2 HOMO of ONQ is shallower than that of OBQ. The above discussion therefore may lead to the conclusion that the $E^{\mathrm{red}}_{1/2}$ of OBQ would shift in a positive direction with the structure change from OBQ to ONQ, this behavior being the same as is usually found in many organic compounds. The aforementioned different behavior between the two series of BQ and OBQ should be entirely due to the different topological natures of the compound systems.

Behavior of Reduction Potentials in the Series of Polyacenes, Polynuclear *p*-Hydroquinones, and Di-*N*-oxides of *p*-Diazapolyacenes

As a typical example showing a normal positive shift of the reduction potential with increasing ring size along the *Z*-axis we here discuss the MO of polyacenes. Some calculation results are listed in Table III, and the MO's of benzene, naphthalene, and BD are shown in Fig. 6, from which it is clear that the LUMO (b_2) and HOMO (a_2) of BD and the LUMO (b_2)

TABLE III. LUMO and HOMO Orbital Energies and Their Orbital Symmetries of the Compounds Listed

Compounds	LUMO energy			HOMO energy		
	PPP	STO-3G	Sym[a)]	PPP	STO-3G	Sym[a)]
o-Benzoquinone	−3.931	3.749	b_2	−10.490	−7.445	a_2
o-Naphthoquinone	−4.412	2.528	b_2	−9.222	−5.284	a_2
o-Anthraquinone	−5.637		a_2	−7.700		b_2
Hydroquinone	−1.133	6.985	$a_2(a_u)$	−9.443	−5.941	$a_2(b_{3g})$
1,4-Dihydroxynaphthalene	−2.223	5.497	b_2	−8.951	−4.956	a_2
5,10-Dihydroxyanthracene	−2.865		$b_2(b_{1u})$	−8.419		$a_2(b_{3g})$
Pyrazine di-*N*-oxide	−3.256	4.470	$b_2(b_{1u})$	−9.679	−4.197	$a_2(b_{3g})$
Quinoxaline di-*N*-oxide	−3.639		b_2	−9.305		a_2
Phenazine di-*N*-oxide	−4.021	3.000	$b_2(b_{1u})$	−8.826	−3.147	$a_2(b_{3g})$
Benzene	−1.230	7.298	$a_2, b_2(e_{2u})$	−10.610	−7.602	$a_2, b_2(e_{1g})$
Naphthalene	−2.367	5.315	$b_2(b_{2g})$	−9.473	−5.837	$a_2(a_u)$
Anthracene	−3.022	4.144	$b_2(b_{1u})$	−8.818	−4.765	$a_2(b_{3g})$
Tetracene	−3.429		$b_2(b_{2g})$	−8.411		$a_2(a_u)$
Pentacene	−3.695		$b_2(b_{1u})$	−8.145		$a_2(b_{3g})$

a) Symmetries under C_{2v} are denoted, those under V_h or D_{6h} being shown in parentheses.

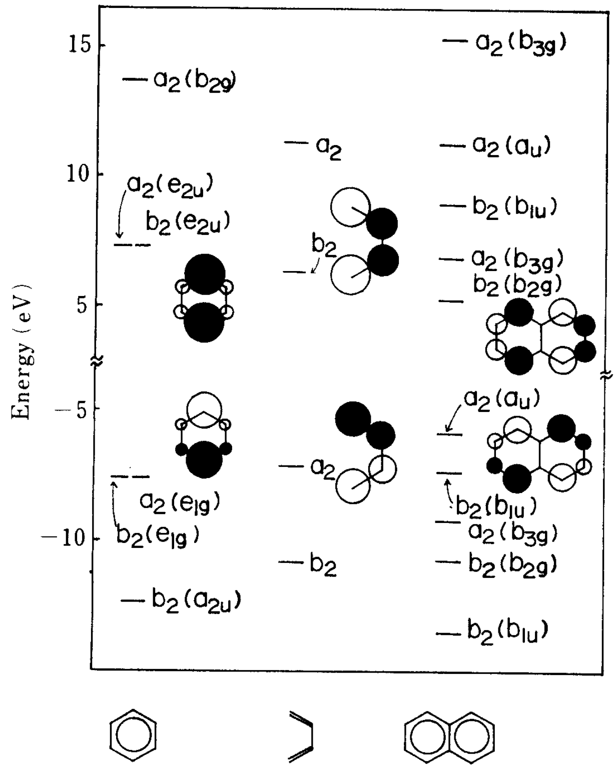

Fig. 6. STO-3G π-MO Energy Levels and the MO Illustration of π-HOMO's and π-LUMO's of Naphthalene and Its Composite System Consisting of Benzene and *cis*-Butadiene

For benzene, MO's are illustrated only for b_2 (e_{2u}) LUMO and a_2 (e_{1g}) HOMO. The axes under C_{2v} and D_{6h} are the same as given for C_{2v} and V_h in Chart 1.

and HOMO (a_2) of benzene are, respectively, similar in energy level, so that each pair of the LUMO's or the HOMO's may interact strongly, resulting in the LUMO (b_2) and the HOMO (a_2) of naphthalene being, respectively, stabilized and unstabilized in comparison with those of benzene. This kind of orbital interaction may always be found with increasing ring size along the *Z*-axis of the hydrocarbons. Therefore the stabilization of the LUMO and the unstabilization of the HOMO necessarily lead to the positive shift of $E_{1/2}^{\text{red}}$ and the negative shift of $E_{1/2}^{\text{oxd}}$ with increasing ring size along the *Z*-axis of polyacenes.[35,36)

Next, let us discuss the case of the two series of *p*-hydroquinone and pyrazine di-*N*-oxide, since these compounds are very interesting in that the number of $2p\pi$ atomic orbitals of these substances is the same as that of BQ, but the former has two extra π-electrons compared with BQ. Figure 7 shows the MO's and their energy levels of 1,4-dihydroxynaphthalene, *p*-hydroquinone (HQ), quinoxaline di-*N*-oxide, pyrazine di-*N*-oxide (PDNO), and BD. The LUMO orbitals of HQ and PDNO consist mainly of two adjacent MO's with a_2 and b_2 symmetry under C_{2v}, and the a_2 MO is completely localized inside the ring portion. The HOMO clearly has a_2 symmetry for both compounds, as can be seen from Fig. 7. These results make it possible to predict that the mutual interaction of the LUMO and HOMO of HQ or PDNO with those of BD is very similar to the interaction of the LUMO and HOMO of OBQ and benzene with those of BD, so that the positive shift of $E_{1/2}^{\text{red}}$ values of the above compounds with increasing π-conjugation can be reasonably understood. The experimental results were reported in our previous papers for the case of aromatic amine *N*-oxides.[12,37,38) The calculation results of the LUMO and HOMO energies for the polynuclear *p*-hydroquinones and di-*N*-oxides of *p*-diazapolyacenes are included in Table III. Now, the two extra π-electrons existing in hydroquinone and pyrazine di-*N*-oxide necessarily have to enter the LUMO of BQ when we use the MO of BQ to construct the MO of the former substances. Thus, the LUMO of BQ turns out to be the HOMO of HQ or PDNO. These circumstances indicate that the change of LUMO energy in hydroquinone with increasing ring size along the *Z*-axis just corresponds to the behavior of the third unoccupied b_2 orbital of BQ (see Fig. 4)

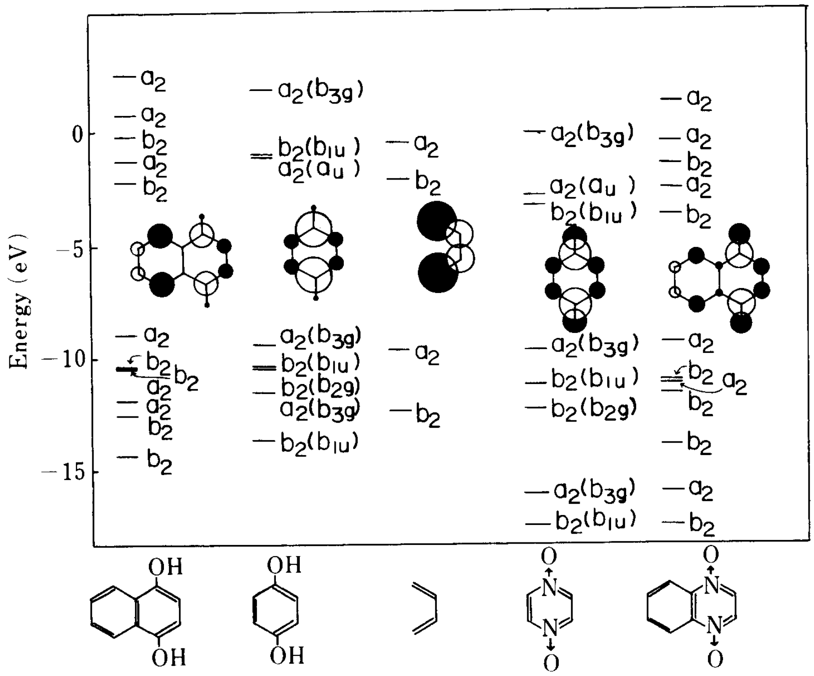

Fig. 7. PPP π-MO Energy Levels and the MO Illustration of b_2 Type LUMO's of Quinoxaline Di-*N*-oxide and 1,4-Dihydroxynaphthalene and Their Composite Systems Consisting of *cis*-Butadiene, Pyrazine Di-*N*-oxide, and Hydroquinone

The axes under C_{2v} and V_h are given in Chart 1.

with the above molecular change, and results in stabilization.[39]

In conclusion, we may say that usual organic substances generally undergo reduction more easily as the π-electron system increases in size as already discussed for some typical compounds, but there are some exceptional substances such as aromatic polynuclear *p*-quinones which show a negative shift of $E^{\text{red}}_{1/2}$ values with the above structure change, though this kind of behavior seems to be rate. The main reason for this exceptional behavior may be summarized as follows. Considering the composite system, just as in the interaction of BQ and BD, let us focus attention on the LUMO energy of any one system (such as BQ), which is located at a quite stabilized position (*i.e.* large electron affinity) but which can not (or can barely) interact with the LUMO of the other system (such as BD) occupying the adjacent position. However, if the interaction of the LUMO of some *p*-quinone substance with the HOMO of BD is effective on the grounds of the orbital symmetry and the perturbation energy values, then the LUMO of *p*-quinone is destabilized, and consequently the $E^{\text{red}}_{1/2}$ value of the *p*-quinone system shifts in a negative direction, as was actually found in the case of the BQ series. These phenomena seem to be mainly due to the characteristic topological nature of the aromatic *p*-quinone series, which may be determined by the number of π-AO's and π-electrons and also by the orbital symmetry arising from the molecular symmetry and the shape. It might be possible to verify the present results analytically by the application of topology, graph and group theories.

Substituent Effect on the Reduction Potential of Anthraquinone

Although the reduction potential, $E^{\text{red}}_{1/2}$, of polynuclear aromatic *p*-quinones behaves abnormally for the structure change discussed hitherto, we should expect normal substituent effects even on the quinone compounds, since the substituent effect is regarded only as a perturbation to some position in the MO.[40] The half-wave reduction potential and the calculated PPP LUMO energies of anthraquinone substituted at the 1st and 2nd positions, and the σ_p substituent constant are shown in Table II. Regression analysis of these data gave the following result: $E_{1/2}^{\text{red}} = -1.393\varepsilon_{1\text{u}} - 5.639$ with the correlation coefficient $(r) = 0.9021$, and $E_{1/2}^{\text{red}} = 0.310\sigma_{\text{p}} - 0.861$ with $r = 0.9866$. We can see from these data that a strongly electron-donating substituent, NH_2, having shallower LUMO energy and quite a large negative value of σ_{p} moves the $E_{1/2}^{\text{red}}$ value of anthraquinone markedly to the negative side. This is the normal behavior, as reported by us and other workers.5,6,41)

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